

TANNING STUDIES WITH DIALDEHYDE STARCH*

E. M. FILACHIONE, E. H. HARRIS, M. L. FEIN, A. H. KORN,
J. NAGHSKI, AND P. A. WELLS

*Eastern Regional Research Laboratory†
Philadelphia, Pennsylvania*

1181

ABSTRACT

Dialdehyde starch, a reactive derivative potentially available at low cost by oxidation of starch, has been shown to have tanning action. Studies were made to determine the effect of such factors as degree of oxidation, method of solubilization, time of treatment, and pH of medium on the rates and degree of tannage.



INTRODUCTION

The tanning action of certain aldehydes, particularly formaldehyde, has been known for some time, and studies have indicated that tanning action is generally limited to the simpler aliphatic aldehydes of low molecular weight (1,2,3). Recent investigations have shown that the reactivity of dialdehydes toward hide substance is not as critically influenced by molecular weight as in the case of the monofunctional aldehydes (4,5,6). This paper is in the nature of a progress report describing our investigations on the tanning action of dialdehyde starch, also referred to as oxystarch, a polyfunctional aldehyde derived from starch by periodate oxidation. Our interest in dialdehyde starch was stimulated by the recent development of an efficient electrolytic process for effecting this oxidation (7,8,9). In this new process the expensive reagent, sodium periodate, is constantly regenerated electrolytically during the reaction, making dialdehyde starch potentially available at low cost.

EXPERIMENTAL

Materials.—The raw stock was pickled calfskin purchased from a local tannery. Dialdehyde starch was supplied by the Northern Utilization Research and Development Division, the dialdehyde content varying from 10 to 98%.

Preliminary tanning studies.—Dialdehyde starch may be dissolved in water either by heat or with alkalis. The tanning properties of solutions prepared by both of these methods were investigated.

*Presented in part at the Fifty-third Annual Meeting of ALCA, Lake Placid, New York, June 2-5, 1957.

†A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

Method A.—The dialdehyde starch was dissolved by autoclaving a 10% suspension in water at 120° C. for ½ hr. The cooled solution was then adjusted to a concentration of 5% with respect to dialdehyde starch and 10% in sodium sulfate. The pH value of these solutions when used for tanning was maintained in the regions of approximately 5, 8, and 10 by the use of acetate, bicarbonate, and mixed bicarbonate–magnesium oxide buffers respectively. Small pieces of drained pickled calfskin, 4" x 6" in size and about 40 g. in weight, were added to 120 g. of the dialdehyde starch solution (3 l float) in bottles which were gently agitated by rolling on a jar mill. Small portions of these specimens were removed after 2, 6, and 24 hr. for determination of shrinkage temperature and leather-like drying after washing for one day. These data are summarized in Table I.

TABLE I
TANNING OF CALFSKIN WITH DIALDEHYDE STARCH (AUTOCLAVED)*

Expt. No.	Dialdehyde Content, %†	Treatment		Shrinkage Temp., °C., After					Leather-like Drying After††
		Buffer	pH‡	2 hr.	6 hr.	24 hr.	72 hr.	Neut.**	
1	95 to 98	HOAc + NaOAc	4.9–5.0	61	72	76	78	—	24 hr.
2	"	0.3M NaHCO ₃	7.3–8.2	74	80	81	83	82	6 "
3	"	1% MgO	9.6–9.5	55	61	79	83	79	24 "
4	"	MgO + NaHCO ₃	9.4–8.9	69	85	86	87	86	6 "
5	71	HOAc + NaOAc	4.9–5.0	—	66	70	74	—	24 hr.
6	"	0.3M NaHCO ₃	7.3–7.8	68	74	81	82	80	6 "
7	"	1% MgO	10.1–10.2	53	63	73	74	70	72 "
8	"	MgO + NaHCO ₃	10.0–9.8	68	80	83	79	77	6 "
9	60	HOAc + NaOAc	5.0	—	66	68	72	—	24 "
10	"	0.3M NaHCO ₃	7.2–7.7	67	72	78	81	79	6 "
11	"	1% MgO	10.2	55	62	69	74	72	72 "
12	"	MgO + NaHCO ₃	9.6–9.4	73	80	83	84	79	2 "
13	29	HOAc + NaOAc	5.0	—	61	62	64	—	>72 "
14	"	0.3M NaHCO ₃	7.1–8.6	63	66	74	82	78	24 "
15	"	1% MgO	10.6–10.4	56	61	68	68	63	>72 "
16	"	MgO + NaHCO ₃	10.6–10.3	72	73	77	76	73	2 "
17	10	HOAc + NaOAc	5.0	—	60	60	62	—	>72 "
18	"	0.3M NaHCO ₃	7.4–8.8	62	61	68	77	73	72 "
19	"	1% MgO	10.6–10.2	53	53	64	63	62	>72 "
20	"	MgO + NaHCO ₃	10.6–9.9	68	67	69	72	65	>72 "

*Tanning solution: 5% solution concentration with respect to dialdehyde starch (solubilized in autoclave); 10% in Na₂SO₄.

†Extent of anhydroglucose units of starch converted to dialdehyde structure.

‡At beginning and end of tanning.

**Sample tanned for 3 days then neutralized in acetate buffer (pH approx. 5) for 2 hr.

††Time of tanning which produced specimen showing leather-like drying.

Method B.—A 10% solution of sodium sulfate in water was prepared and sufficient sodium bicarbonate or magnesium oxide (or mixtures of these two

alkaline agents) added to make the solutions 0.3M in NaHCO₃ and/or 1% MgO. To 120 g. of such a solution was added 6 g. of solid dialdehyde starch and one piece (4" x 6") of drained pickled calfskin. Agitation was provided by carrying out the treatment in bottles rolled on a jar mill. The dialdehyde starch gradually dissolved during the earlier stages of the treatment. The results are tabulated in Table II.

TABLE II
TANNING OF CALFSKIN WITH DIALDEHYDE STARCH (DRY)*

Expt. No.	Treatment			Shrinkage Temp., °C., After					Leather-like Drying After††
	Dialdehyde Content, %†	Buffer	pH‡	2 hr.	6 hr.	24 hr.	72 hr.	Neut.**	
1	98	0.3MNaHCO ₃	7.5-8.2	64	73	81	83	83	24 hr.
2	"	MgO, 1%	9.5-9.4	53	66	81	84	80	24 "
3	"	MgO + NaHCO ₃	9.5-8.8	80	83	86	87	85	2 "
4	71	NaHCO ₃	7.4-7.8	63	70	80	82	80	24 "
5	"	MgO	10.3-10.2	59	63	71	75	74	72 "
6	"	MgO + NaHCO ₃	10.8-8.8	74	77	82	83	79	2 "
7	60	NaHCO ₃	7.3-8.0	62	78	81	84	83	6 "
8	"	MgO	9.5-9.6	57	60	73	77	74	24 "
9	"	MgO + NaHCO ₃	9.3-9.0	76	78	87	85	86	2 "
10	29	NaHCO ₃	7.4-8.6	67	71	79	85	83	24 "
11	"	MgO	9.6-9.8	63	63	66	69	70	72 "
12	"	Mg + NaHCO ₃	9.4	74	82	86	83	79	6 "
13	10	NaHCO ₃	7.3-8.9	64	66	74	80	78	24 "
14	"	MgO	9.7-9.9	55	62	65	66	64	72 "
15	"	MgO + NaHCO ₃	10.3-9.8	66	72	70	70	67	6 "

*Tanning solution: 5% on solution basis with respect to dialdehyde starch (added dry); 10% in Na₂SO₄. For other footnotes, see Table I.

Tanning full calfskins.—Into a drum (16½" wide and 5' inside diameter) 10.6 l. of water, 1.38 kg. of Na₂SO₄, and 0.17 kg. of NaHCO₃ were charged and dissolved. Two drained pickled calfskins, amounting to 5.3 kg., were added to the drum, which was then run for 1 hr. At the end of this time the pH was 7.4, and an additional 0.23 kg. of NaHCO₃ was added followed by 0.53 kg. of solid dialdehyde starch of 95% dialdehyde content. Drumming was continued for 7 hr. After resting overnight (16 hr.) the contents were drummed for an additional 2 hr. At the end of this time the solution, which had an amber color, showed a pH of 8.3, and the T_s of the leather was 79° C. (T_s of a specimen after 7 hr. of tanning was only 66° C.) The contents of the drum were then acidified by adding a total of 0.12 kg. of 80% formic acid in four feeds with 1 hr. of drumming after each feed. The drum rested overnight (pH of the liquor was 4.4), then the tanned skins were washed for 3 hr. The dialdehyde starch-tanned calf-

TABLE III

EFFECT OF pH AND DEGREE OF OXIDATION ON THE FIXATION OF DIALDEHYDE STARCHES BY CALFSKIN

Expt. No.	Tannage*	pH	Ts.°C.	Total N	Analysis, % (MFB)			Fixed Aldehyde	
					Fat	Ash	Hide Subs. N X 5.62	% by wt †	% of H.S.
1	Dialdehyde starch, 95% oxid., autoclaved	6.9	80	16.08	0.38	1.23	90.37	8.0	8.9
2	" " 60% " "	7.0	78	16.52	0.37	0.89	92.84	5.9	6.4
3	" " 44% " "	7.1	74	16.82	0.18	0.73	94.53	4.6	4.9
4	" " 95% " "	9.6	84	16.42	0.30	1.55	92.28	5.9	6.4
5	" " 60% " "	9.7	83	16.61	0.24	1.76	93.35	4.7	5.0
6	" " 44% " "	9.9	79	17.06	0.20	1.33	95.88	2.6	2.8
7	Dialdehyde starch, 95% oxid., dry	7.0	82	16.07	0.23	1.16	90.31	8.3	9.2
8	" " 60% " "	7.2	78	16.30	0.19	1.06	91.61	7.1	7.8
9	" " 44% " "	7.5	77	17.11	0.11	0.77	96.16	3.0	3.1
10	" " 95% " "	9.5	82	16.66	0.27	1.56	93.63	4.5	4.8
11	" " 60% " "	9.7	85	16.40	0.20	2.01	92.17	5.6	6.1
12	" " 44% " "	10.1	80	16.92	0.20	1.76	95.09	3.0	3.2
13	Glyoxal	6.7	80	17.48	0.12	1.18	98.24	0.5	0.5
14	" "	9.1	88	17.16	0.24	1.63	96.44	1.7	1.8
15	Untanned, acetone-dehydrated		60	18.05	0.23	0.85	101.44	(-2.5)	

*Concentrations of tanning solutions: 5% for dialdehyde starch, 1.8% for glyoxal; all 10% in Na₂SO₄.
 †Calculated from balance on MFB; i.e., 100 minus (hide substance + fat + ash).

skin was smooth-grained and showed a shrinkage temperature of 79° C. A sample without fatliquor, dried at room temperature, was almost white and showed good leather characteristics.

This tannage was also carried out at a higher pH (9 to 10) by substantially the same process as described above except that a mixture of magnesium oxide and sodium bicarbonate was used instead of sodium bicarbonate alone (0.14 kg. of MgO in addition to the NaHCO₃, prior to the addition of the solid dialdehyde starch in the example above). Tanning at this higher pH was more rapid (Ts after 4 hr. was 83° C.), the leather was tan in color, and the Ts of the 24-hr. specimen was 86° C. (lowered to 82° C. after acidification).

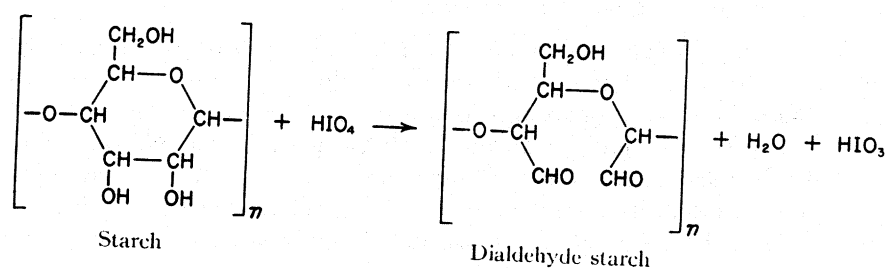
Fixation of dialdehyde starch.—For purposes of analysis pickled calfskin was depickled in sodium acetate-acetic acid buffer, washed, and then dehydrated in several changes of acetone. Pieces of the acetone-dehydrated skin, amounting to about 65 g., were wet back in water for 6 hr., wrung (wrung weight 165 g.), and then tanned for one day with various dialdehyde starches under different conditions as indicated in Table III. After tanning, the leather was washed for one day, air-dried, and ground in a Wiley mill. Moisture, fat, and ash were determined by standard methods (10) and total nitrogen by the semimicro method (11). Fixed aldehyde was calculated as the difference between 100 and the sum of hide substance, fat, and ash on a moisture-free basis. The results are summarized in Table III.

For purposes of comparison, lots of the calfskin (165 g. on wet-wrung basis) were tanned with commercial glyoxal under conditions comparable to the tannage with dialdehyde starch. The tanning solution (312 ml.) contained 18.5 ml. of commercial glyoxal solution of 30% concentration, 33 g. of anhydrous sodium sulfate, and 5.5 g. of sodium bicarbonate. The treatment was carried out for one day, and the pH was 6.7. Tannage with glyoxal at pH 9.1 was carried out by the same procedure except that 3.3 g. of magnesium oxide were used in addition to the sodium bicarbonate. The concentration of glyoxal in the tanning solutions was about 1.8%, in comparison with about 5% for the dialdehyde starch, in order to compensate for the lower molecular weight of glyoxal. The washed, air-dried pieces were then analyzed, and the data included in Table III.

DISCUSSION

Dialdehyde starch is a polymeric aldehyde derivative formed by the oxidation of starch with periodic acid. Periodic acid oxidation offers a specific means for cleavage of α -glycols and has been advantageously used by organic chemists to elucidate the structure of polyhydric alcohols, e.g., starch itself. The following equation illustrates the reaction as applied to starch. In this

oxidation glucose residues of starch are oxidized to a dialdehyde structure as shown below.



The extent of oxidation can be readily controlled, and a complete range of aldehyde derivatives of starch is made available as the oxidation level varies between 0 and 100%. At 100% oxidation each glucose residue is converted to the dialdehyde structure; at 50% oxidation half of the glucose residues are so altered. Dialdehyde starch is thus an open chain polymer containing aldehyde groups and, if no other bond rupture occurs, should have a molecular weight comparable to the starch from which it is made.

The data in Tables I and II demonstrate the tanning action of dialdehyde starch. Comparable results were obtained whether the dialdehyde starch was first dissolved by autoclaving at 120°C. for ½ hr. or added as the solid directly to the alkaline solutions in which tanning was effected. With the latter procedure a somewhat higher shrinkage temperature was obtained, particularly with the dialdehyde starch of lower oxidation levels. Tanning with the solid dialdehyde starch at pH 7 to 8 was slower than with the autoclaved, probably because the solid material dissolved slowly at this pH. In the drum tanning this was advantageous since it provided an automatic means for the gradual increase of aldehyde concentration in the tanning solution and facilitated the production of a smooth-grained leather.

The data of Tables I and II show that tanning action was not limited to the derivative in which substantially all the anhydroglucose units of the starch were oxidized to the dialdehyde structure. At pH of 7 to 8 practically the same maximum shrinkage temperature (T_s about 80°C.) was eventually attained with the starches ranging from 98 down to 29% in dialdehyde content; however, the rate of tanning decreased with decreasing dialdehyde content. The tanning action of starch of 10% dialdehyde content was extremely poor as indicated not only by the lower T_s but also by the appearance of the treated specimens.

An interesting feature of the data in Tables I and II is the comparison of the magnesium oxide system with a mixture of this oxide and sodium bicarbonate to control the pH. Even though the pH values of these two systems were substantially the same, the latter system resulted in a much more rapid tanning action and was preferable to the former.

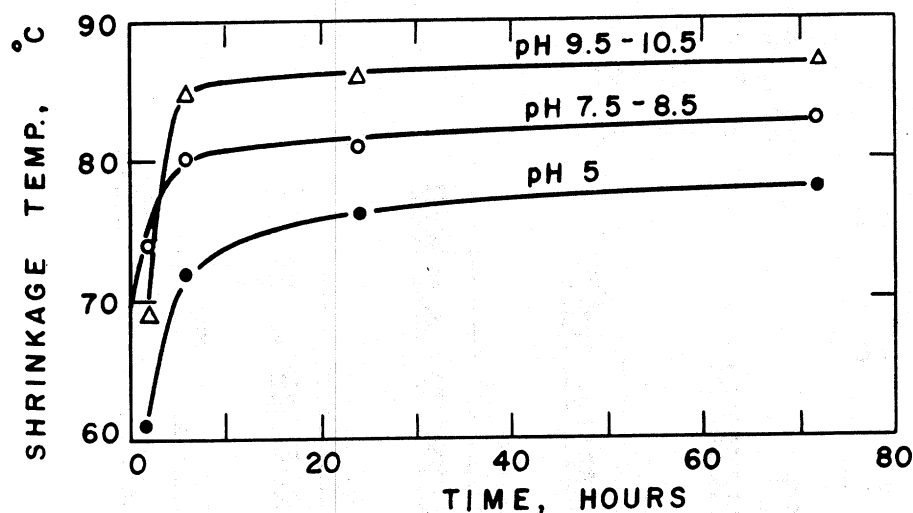


FIGURE 1.—Rate of increase in shrinkage temperature in tanning calfskin with autoclaved dialdehyde starch (95% dialdehyde content).

Figure 1 shows the rate of increase of shrinkage temperature upon tanning calfskin with the autoclaved dialdehyde starch of 95% dialdehyde content. In common with other aldehydes the rate of tanning increased with increasing pH. The maximum T_s also increased with pH and was essentially reached in 6 hr. in alkaline solutions and in 24 hr. in slightly acidic medium. In general, shrinkage temperatures of approximately 78°, 81°, and 86° C. were attained in 24 hr. at pH of about 5, 8, and 10 respectively.

Correlation of the shrinkage temperature after 24 hours of treatment (autoclaved dialdehyde starch) with extent of oxidation of the starch is shown in Figure 2. At pH 5 there is a marked lowering of the 24 hr. T_s with decreasing extent of oxidation. In alkaline solutions the lowering of T_s is not so pronounced until the extent of oxidation falls below 60%. As can be seen from Figure 1, the tanning action of the dialdehyde starch of 10% dialdehyde content was considered poor when used under the conditions of our experiments. In general more favorable leather characteristics were obtained as the dialdehyde content of the starch increased, and from our studies thus far the dialdehyde starch that is almost completely oxidized to the dialdehyde structure seems to be the most suitable material as regards tanning action.

The fixation of aldehyde and comparison with the simplest dialdehyde, glyoxal, were of interest in this study. Methods for the direct determination of these aldehydes are not presently available, hence the fixed aldehydes were determined by difference. The data in Table III show a decreasing fixation of aldehyde with decreasing dialdehyde content of the dialdehyde starch. Perhaps the explanation lies in the fact that although the dialdehyde

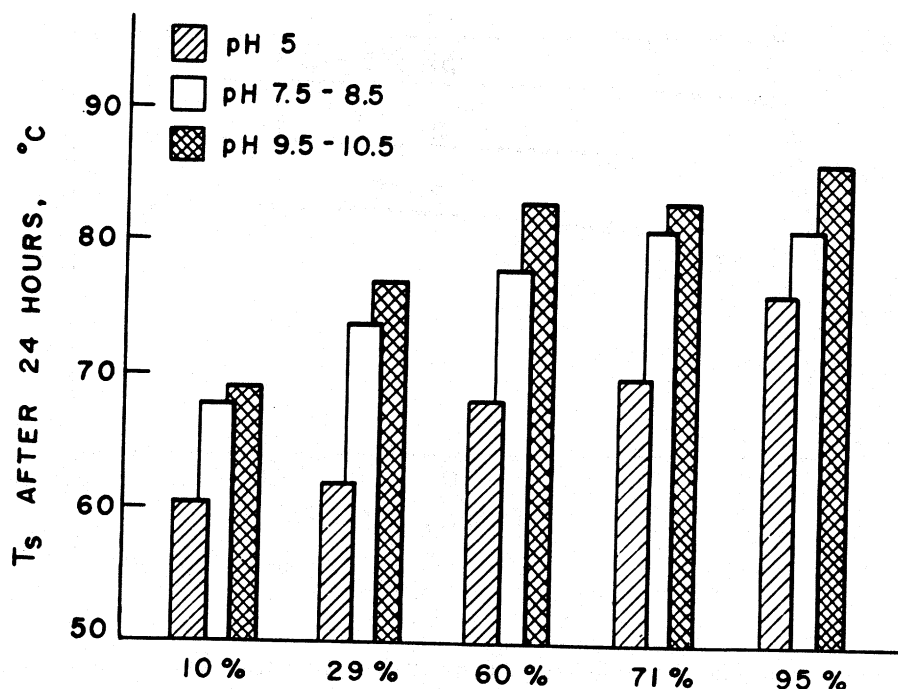


FIGURE 2.—Shrinkage temperature of calfskin treated 24 hr. with autoclaved dialdehyde starch of different degrees of oxidation at 3 pH levels.

starch solutions were all comparable on a solids basis (5% by weight), they are not comparable in concentration on an equivalent aldehyde basis. In contrast to glyoxal, fixation of dialdehyde starch was less at pH 10 than at pH 7, and this may indicate that less dialdehyde starch is needed in tanning at the higher pH. Of interest is the fact that at pH 7 fixation of dialdehyde starch was considerably higher than fixation of glyoxal. However, the fixation was not as high as expected from a derivative of a substance of such high molecular weight as starch, and it appears probable that depolymerization of the dialdehyde starch molecule is a complicating factor in this reaction.

Preliminary experiments have indicated that dialdehyde starch-tanned leather can be retanned with conventional mineral and vegetable tanning agents.

SUMMARY

Dialdehyde starch has been shown to have tanning action. The tanning action varied with the extent of oxidation of the starch. The reactivity and fixation decreased with decreasing level of oxidation, and in general the most promising leathers were obtained using dialdehyde starch of high aldehyde content. In common with other aldehydes, tanning with dialdehyde starch

in the acid range was slower than in the alkaline region. Tanning of calfskin was complete in a period of 6 to 24 hr. and the shrinkage temperature of the leather was 80° and 86° C. when tanned at pH 8 and 10 respectively.

ACKNOWLEDGMENT

The authors wish to express their gratitude to W. Windus for suggestions and constructive criticism, and to staff members of the Northern Utilization Research and Development Division, United States Department of Agriculture, Peoria, Illinois, for supplying the samples of the dialdehyde starch used in this investigation.

REFERENCES

1. Gustavson, K. H. *The Chemistry of Tanning Processes* (New York: Academic Press, Inc., 1956) pp. 244, 278.
2. ———. *J. Intern. Soc. Leather Trades' Chemists*, **24**, 377 (1940).
3. ———. *Svensk. Kem. Tid.*, **59**, 98 (1947).
4. ———. *Ibid.*, **61**, 114 (1949).
5. Seligsberger, L., and Sadler, C. *JALCA*, **52**, 2 (1957).
6. Fein, M. L., and Filachione, E. M. *JALCA*, **52**, 17 (1957).
7. Dvonch, W., and Mehlretter, C. L. *J. Am. Chem. Soc.*, **74**, 5522 (1952); U. S. Pat. 2,648,629, August 11, 1953.
8. Mehlretter, C. L., Rankin, J. C., and Watson, P. R. *Ind. Eng. Chem.*, **49**, 350 (1957).
9. ———. U. S. Pat. 2,713,553, July 15, 1955.
10. ALCA Provisional Methods, May 1954.
11. Willits, C. O., and Ogg, C. L. *J. Assoc. Offic. Agr. Chemists*, **33**, 179 (1950).

Received October 31, 1957.

DISCUSSION

DR. LOLLAR (Tanners' Council Laboratory, University of Cincinnati): I wish to express my own and, I am certain, your thanks, to Dr. Filachione for his very interesting paper evaluating this relatively new material which certainly seems to have some potentialities for our industry.

Although the material was referred to as a dialdehyde starch, I wonder if we should not consider the fact that it is really a polyfunctional material, since because of its molecular weight, there are more than two aldehyde groups per molecule. This might explain its potential tanning function. I can indicate to you from our studies on the use of dialdehyde starch as a reactive aldehyde on keratins that it is truly a material with considerable aldehyde functionality and potential value as a modifying agent for proteins.

I think that the leather will speak for itself, and I trust that you will take an opportunity to look at it.

I was particularly interested in the success achieved with the dry addition of the material. In our work with the material on keratin we have found that

the dissolving of the material is one of the limitations of its use from a practical standpoint. The fact that it works by adding the dry material would be of considerable advantage in the practical application of this material in the tannery.

BORIS MONSAROFF (Hamilton, Ontario): It seems to me that in other carbohydrates such as cellulose there is the possibility of application here. Did you ever try out oxycellulose?

DR. FILACHIONE: No, we have not. The term oxycellulose may be applied to various types of oxidized cellulose. We would be interested in a periodate oxidized cellulose but we know of no one who has it available.

MR. MONSAROFF: Dr. Purvis of Montreal has done work on the periodate oxidation of cellulose rather than starch. I would like to find out if other carbohydrates such as cellulose would have potential application.

DR. FILACHIONE: The periodate oxidized cellulose would be similar to periodate oxidized starch. It should have the same possibilities.

MR. MONSAROFF: You have not tried it?

DR. FILACHIONE: No.

MR. LOTZ (Albert Trostel & Sons Co.): In treating your calfskin squares you started from pickled stock and then depickled. Would you have gotten an improvement in your leather if you had skipped the pickling step entirely and started from the high pH of the bating step?

DR. FILACHIONE: We have not carried out experiments starting with the bated stock. We used the pickled stock because it was convenient to purchase and store it in that state.

MR. LOTZ: It might be interesting to skip the pickling entirely and start with bated stock, thus starting at pH 8 to 9.5, which fits the region in which you are working.

DR. FILACHIONE: It would be interesting to try.

DR. LOLLAR: The drum depickling operation is a tricky operation and you certainly would hesitate to try to do something like that from a practical standpoint if you did not have to.

DR. FILACHIONE: We have carried out the treatment using the pickled stock and just adding the bicarbonate in excess of the amount required for depickling, and then adding the dialdehyde starch. So we don't have to wait actually for a depickling operation. We can carry it out all in one step.

DR. LOLLAR: In that regard, I wonder if you have any indication that there is any reaction, even at more acid pH values than those you reported here? In our keratin work we have found evidence of reaction between the oxystarch and protein at a pH as low as 3.

DR. FILACHIONE: No, we have not gone to very low pH's. I think our lowest pH was in the neighborhood of 3.6, which is the pH of the autoclaved dialdehyde starch.

JEROME J. RITTER (Rohm & Haas Co.): Did you try any of these experiments at higher temperatures in the tanning? And also, does this product have any of the odor drawbacks that regular formaldehyde does?

DR. FILACHIONE: No, we have not tried this at other than room temperature. With regard to odor, there is hardly any odor at all. There is a very slight odor, but nothing that is objectionable or irritating.

MR. RITTER: Would you classify the leather as comparable to straight formaldehyde leather?

DR. FILACHIONE: Oxystarch is similar to formaldehyde in that we have an aldehyde tannage. The leathers are comparable in stability on the alkaline side. However, oxystarch gives a considerably higher fixed aldehyde content than does formaldehyde, and the former produces a fuller leather.

DR. J. H. HIGHBERGER (United Shoe Machinery Corp.): Do you have quantitative data about the amounts of starch fixed?

DR. FILACHIONE: Yes, we have. The leathers were analyzed for total nitrogen, fat, and ash, and fixed aldehyde was calculated by difference. Fixed aldehyde was about 8% on an analytical basis.

DR. HIGHBERGER: Is that the maximum?

DR. FILACHIONE: Our highest was 8.3%. It is interesting that the weight gain, based on conditioned samples, was about 11%.

ADOLF SCHUBERT: Is the material being produced at the present time?

DR. FILACHIONE: As far as I know, it is not being produced commercially at the present time. Our samples were supplied by the Northern Utilization Research and Development Division, U. S. Dept. of Agriculture, Peoria, Ill. They developed the new electrolytic process for the preparation of this material and probably are able to supply small samples.

DR. LUDWIG SELIGSBERGER (Quartermaster Research and Engineering Center): I would like to caution against using higher temperatures, particularly at higher pH values. I think Dr. Filachione may also have found

that the material is not too stable at a pH of around 8.5 or 10 and disappears in solution gradually when used for tanning. I would say for this reason that maybe it would be advisable to add it in several feeds and not to add the dry material all at once.

DR. FILACHIONE: Thank you. That is interesting.

JAMES KELLY (Ellithorp Tanning Co.): Was there any special procedure used in tanning these sample skins?

DR. FILACHIONE: This was tanned in our laboratory and then processed through a tannery with a regular pack.

MR. KELLY: Were the skins treated with sulfonated oil or cationics?

DR. FILACHIONE: I have no specific information with regard to the fat liquor.

DR. LOLLAR: As far as you know, no modification was made of the process customarily used in that calfskin tannery?

DR. FILACHIONE: That is correct.

C. DAVID WILSON (Fred Rueping Leather Company): What would you expect the color of this leather to be, had it not been dyed?

DR. FILACHIONE: Tanning at pH 8 gave a somewhat off-white leather, while tanning at pH 10 produced a tan-colored leather.

CHARLES W. MANN (Quartermaster Research and Engineering Center): Dr. Filachione was kind enough to let us have a sample of his material to use in connection with our research. We were conducting a series of tests on heavy leather, attempting to make sole leather by first tanning with aldehyde and after stabilizing the fiber in this manner, adding filling materials. We made a tannage with dialdehyde starch, and under conditions where we used about 1.5 to 2 normal carbonate solutions and then reacidified to a pH of 5, we got overnight tannage that was very satisfactory. We had no difficulty whatever except, as Dr. Seligsberger pointed out, we did add material in several feeds. But the tannage was satisfactory. The leather had a very good color and compared favorably with the other leathers we had.

After we filled it with conventional vegetable tanning materials, adding weight and solidity to it, it was rated very satisfactory by the tanners as compared with ordinary sole-type leather. Dr. Filachione has a sample of that leather, and I think he will agree it is good quality.

DR. FILACHIONE: Yes. I might point out that this dialdehyde starch is quite sensitive to alkali. We tried to run the pH up beyond 10 by using lime,

but the pH came down to 6 or 7. We were unable to maintain the pH at about 12.

H. A. TETREAU (A. C. Lawrence Leather Co.): Did you find that this material was extremely hygroscopic?

DR. FILACHIONE: Yes, this leather does absorb water quite rapidly.

WILLIAM J. McDERMOTT (Rohm & Haas Co.): At your higher pH values do you find that you get further oxidation of the aldehyde, especially in the presence of the alkaline earth metals such as calcium or magnesium, which might account for your change in color going more toward the brownish?

DR. FILACHIONE: We really don't know.

MR. McDERMOTT: I wondered if some of the aldehyde group went further than the carboxyl, or whether you get some form of condensation as in the case of formaldehyde.

DR. FILACHIONE: There is some question about what happens to dialdehyde starch in alkaline solutions, and the chemistry involved is largely unknown.

MR. McDERMOTT: Have you done anything on retannages?

DR. FILACHIONE: Yes, we have carried out preliminary experiments on combination tannages, mainly retannage with chrome, alum, and vegetable tannins. It seems to be straightforward and comparable to other aldehyde tannages as regards combination tannages.

JOSEPH N. ORIETAS (Albert Trostel & Sons Co.): I wonder if you have run any aging tests on the finished leather, and how such a leather would behave during storage?

DR. FILACHIONE: No, we have not. We have heated some of this leather in an oven at 90° to 100°C. for a period of a day, and the shrinking temperature goes down under these conditions.

DR. LOLLAR: From a chemical standpoint it has been our observation that the reaction between the dialdehyde starch and the protein yields a product rather typical of the other aldehyde tannages. I would expect, as a first approximation, that this might function very similarly to formaldehyde—maybe a little more like glyoxal—from a chemical standpoint.

DR. FILACHIONE: From the standpoint of response to ultraviolet light, leather tanned with dialdehyde starch behaved similarly to glyoxal-tanned leather, that is, both were bleached.
